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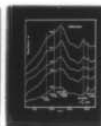
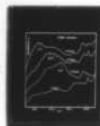
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by

George B. Rouse, Andreas T. Tsatsas, Adi Eisenberg and

William M. Risen, Jr.

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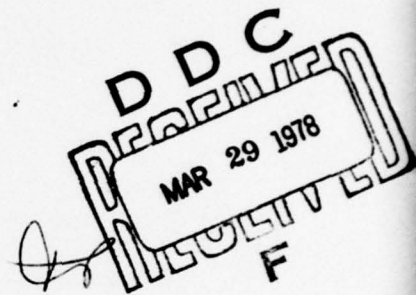
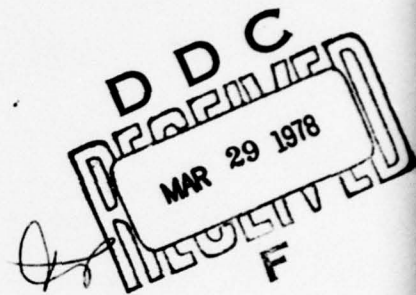
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<p>Direct evidence for the existence of ion clusters in ionomers has been found through the investigation of the far infrared spectra of (PSMA) alkali metal ionomers of polystyrene methacrylic acid measured as a function of ionic content. The Co existence of two kinds of cation-containing environments, multiplets and clusters, has been shown for sodium PSMA ionomers, in which the two must be present simultaneously above 3.9 mole % of ionic groups. The study includes H^+, Na^+, Cs^+, and Ba^{+2} PSMA ionomers in the 50-500 cm^{-1} region.</p>		

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Far Infrared Studies of Ion Clustering in Ionomers

by

George B. Rouse¹, Andreas T. Tsatsas², Adi Eisenberg³
and William M. Risen, Jr.^{1,4}

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Introduction

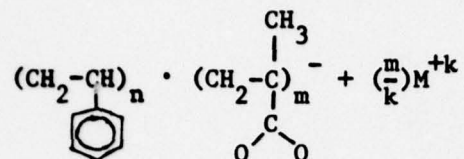
The state of aggregation of ionic groups in solid state ionomers, ion-containing polymers, is known to be important in determining the mechanical and rheological properties of the materials. These materials usually are formed by replacing the H^+ ions in acidic copolymers, such as polyethylene methacrylic acid copolymers, by metal ions. In materials of low dielectric constant and at low ionic concentration, the ions (metal ions and ionic sites on the polymer) aggregate to some degree to form ion-pairs and multiplets (several ion pairs) which act as transient crosslinks. As the concentration of ionic groups increases many of the ions, along with some non-ionic material, come together to form larger clusters. These clusters act not only as crosslinks but also as re-enforcing fillers of microcrystallites. Clearly, then, the physical properties of such ionomers not only are very different from those of the related non-ionic polymers but are dependent on the ionic concentration.

Eisenberg⁵⁻⁷ and others⁸⁻¹⁰ have reviewed the physical properties of ionomers and the extensive studies concerning ionomers and their formation of multiplets and clusters. No vibrational spectroscopic evidence for the existence of the clusters has been reported.

Based on our previous experience with non-aqueous electrolyte solutions¹¹, polyethylene methacrylic acid ionomers¹² and ionic glasses¹³, we have used far infrared spectroscopy to probe cation-cation and cation-site interactions in polystyrene methacrylic acid ionomers as a function of cation and ion-site concentration in an attempt to identify spectroscopic evidence of domain formation. More specifically the attempt is to identify a far infrared band due to the vibration of a higher order cluster.

Experimental

Polystyrene methacrylic acid (PSMA) ionomers, of the form



where M^{+k} is Na^+ , Cs^+ or Ba^{+2} were prepared by the methods of Eisenberg and Navratil.¹⁴ Labelling of materials is by a number giving the mole % of methacrylic acid comonomer followed by letters (H, Na, Cs, Ba) in parentheses indicating the acidic or metalated copolymer and with the letter l or h to indicate low (50,000-70,000) or high (ca 400,000) molecular weight respectively. For example, 4.6 (Na)h is the sodium-form ionomer of the PSMA copolymer with 4.6 mole % acid groups and a molecular weight of about 400,000. Table I gives the acid concentrations of the samples studied in mole %, n/m ratio and in terms of carbon atoms between acid groups for the PSMA ionomers. The degree of replacement of carboxylic hydrogens by M^{+k} was 99-100% in the samples studied. This can be ascertained from the mid-infrared spectra of the ionomers.

The far infrared spectra in the region $50-450 \text{ cm}^{-1}$ of 0.05-0.20 mm thick films of PSMA ionomers were recorded with a Digilab FTS-14 Fourier transform far infrared spectrometer at ambient temperature. Each spectrum was recorded several times with a reproducibility of 1% in absorbance and with ca. 2 cm^{-1} resolution.

Spectral Results

The far infrared spectra ($50-450 \text{ cm}^{-1}$) of the low molecular weight PSMA ionomers containing Cs^+ , Ba^{+2} and Na^+ and the un-ionized form of the low molecular weight copolymer are shown in Figure 1. A dominant feature appears in

the Cs^+ , Ba^{+2} , and Na^+ ionomer spectra which is not present in the spectra of the un-ionized form in the region below 300 cm^{-1} . This feature is a broad, well defined band which shifts from $250 \pm 5 \text{ cm}^{-1}$ for the Na^+ ionomer to $185 \pm 5 \text{ cm}^{-1}$ for Ba^{+2} , to $115 \pm 5 \text{ cm}^{-1}$ for Cs^+ . Since these bands shift strongly with cation mass and charge, they must be due to cation-site vibrations and are assigned to cation motion in the anionic field of the copolymer¹².

In Figure 2 are shown the spectra of a series of Na^+ -form PSMA ionomers in which the anionic-group (acid) concentration is varied. As this concentration increases a band appears at ca. 170 cm^{-1} on the low frequency side of the main Na^+ -motion band. In the band structure observed between 150 and 300 cm^{-1} there are three bands. The one at about 250 cm^{-1} is the primary cation motion band and, since it is present and dominant at low ionic concentration, it is assigned to the vibration of an aggregate involving few ions (low order multiplet). The middle of the three bands at ca 220 cm^{-1} , is a weak internal mode of the polymer. The 170 cm^{-1} band is assigned to the vibrations of aggregates involving many cations and anionic sites close together.

This is entirely consistent with the formation of higher aggregates or clusters, because the oscillations of cations in such ion domains should have both a larger effective mass and lower effective force field (since the cation-anion site attraction becomes increasingly screened). Thus, the vibrational frequency becomes lower than that of the simple cation-site or multiplet oscillators, which is consistent with a previous observation⁷ that in solution the ion motion frequencies for simple ion pairs is higher than that for higher aggregates.

All PSMA samples have a band at 405 cm^{-1} which is of constant intensity after suitable corrections are made to account for varying sample thickness. This indicates that the band is due to a vibration along the polymer backbone since it is independent of ion content of the polymer. It might be assigned to either an out-of-plane bend of the benzene-type six-membered ring, as the one occurring at 405 cm^{-1} in polystyrene, or to a C-C-C bend along the polymer chain. In straight chain alkanes the C-C-C bend is observed in the $350\text{--}450\text{ cm}^{-1}$ frequency range¹⁵.

The constancy of the 405 cm^{-1} band is significant in light of the appearance of another band at 386 cm^{-1} in the Na^+ ionomer, 387 cm^{-1} in the Ba^{+2} and 381 cm^{-1} in Cs^+ . This band is absent in the acid form, is not observed in the 0.6 (Na)& sample, but increases in intensity as the ion concentration increases (see Figure 2), which suggests that the vibration giving rise to this band is associated with the anion site. Two vibrational modes, clearly coupled, which meet this criterion, are C-C-O and the O-C-O bending motions, both modes of the carboxylate group.

Discussion

It is clear from the interpretation of the far infrared data that as the concentration of ionic sites increases the cation finds itself in more than one kind of environment. If at very low ionic site concentrations the sodium ion and the carboxylate ion form low order multiplets involving 1-4 cations plus anionic sites, the vibration of the cation in the force field of the anion and the hydrocarbon backbone give rise to the band at ca 250 cm^{-1} . With increasing ionic concentration, and much the same way as occurs in solution, higher aggregates are formed.

Whether the higher order aggregate band at 170 cm^{-1} should be assigned to vibrating clusters,¹⁶ or "ion drops", as defined by Holliday⁹, or other specific higher order aggregates cannot be asserted from our results. This is true despite the fact that it might be attractive to assign the 170 cm^{-1} band to vibrating ion drops because it is observed even for low (3.8 and 4.6 mole %) ion concentrations. Rheological, small angle X-ray scattering and time-temperature superposition evidence for clustering is apparent at ionic concentrations greater than 6 mole % for PSMA ionomers. However, our spectroscopic method may be more sensitive in detecting the existence of clusters than the above techniques and it detects them as they form and increase in concentration even before they become important rheologically.

Within the vibrating higher order aggregate repulsions between mobile cations tend to alter the force field felt by the cation and cause low frequency ion motion vibrations. Interactions between cations adjacent to the carboxylate sites and these sites themselves are not greatly affected by this aggregation since the carboxylate band in the 400 cm^{-1} region is not shifted.

The principal driving force for the formation of ion aggregates is the low dielectric constant of the backbone since the interionic attraction per cation changes little as aggregation proceeds. Whenever distances between ions are small enough, this driving force causes higher aggregates to be formed. The spectroscopic evidence, therefore, is consistent with the proposition⁶ that at low ionic concentrations small ion aggregates are formed, but at higher concentrations clustering of such aggregates to form ionic domains predominates.

Acknowledgements

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16. The term "cluster" implies ion-rich regions alternating with ion-poor regions. MacKnight¹⁷ et al. has proposed a model consisting of a large central multiplet (ionic region) coated with a non ionic skin and surrounded by other multiplets or ion pairs. Eisenberg's model is that of a collection of interacting

multiplets separated by non-ionic material. (See references 7 [p. 31] and 9 [pp 30-36].)

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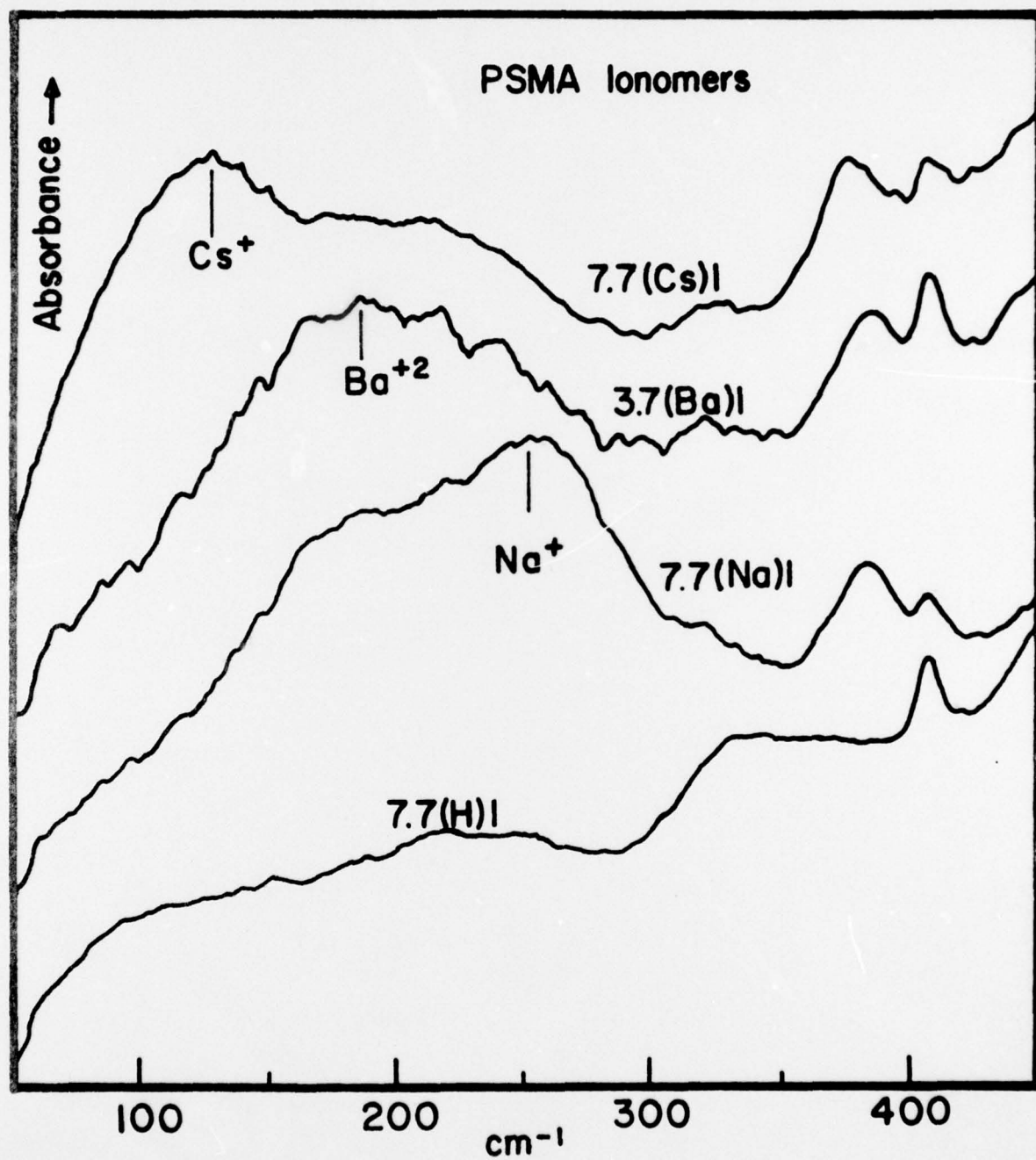
Table I. Acid Concentrations and Average Number of Carbon Atoms Between
Acid Groups (\bar{a})

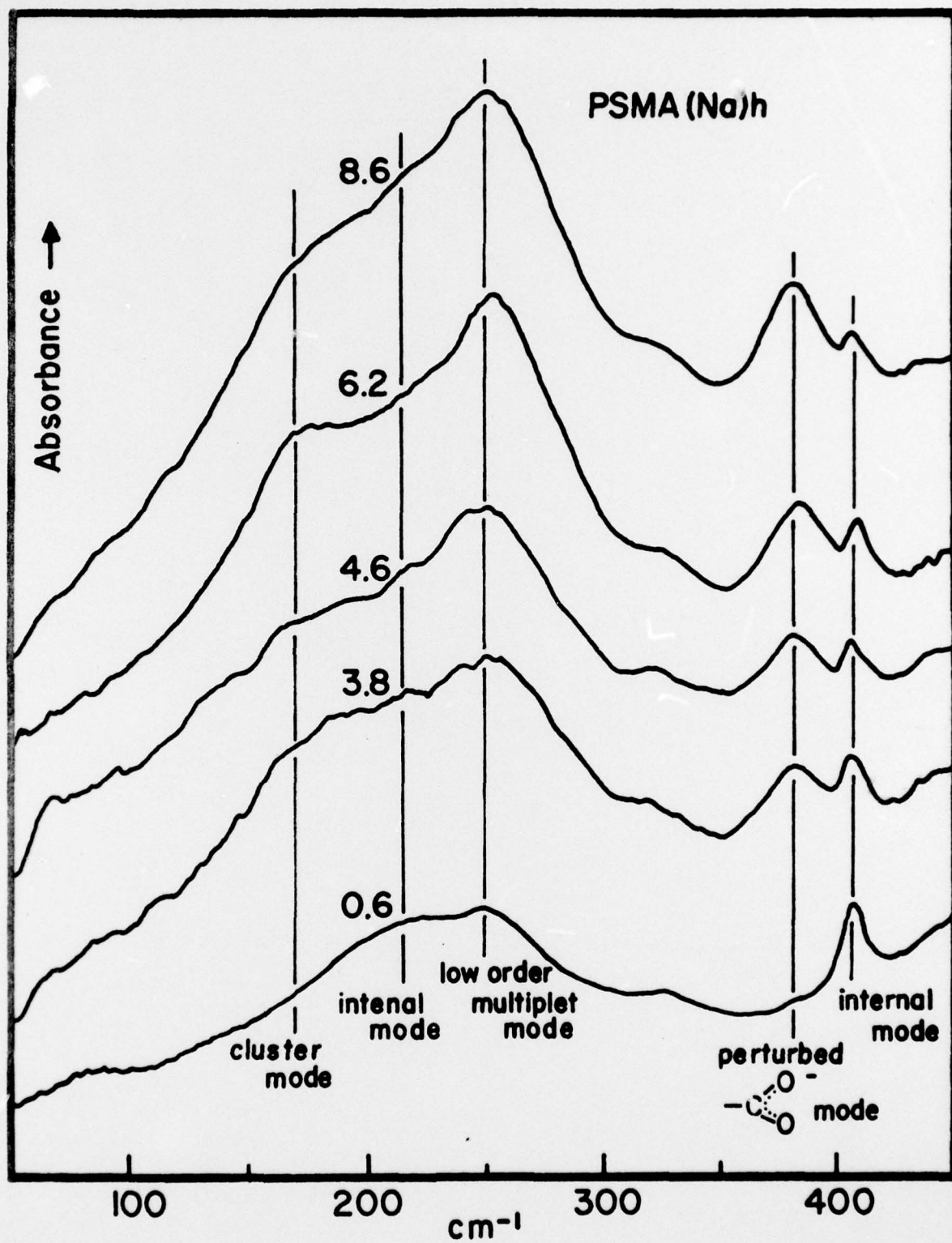
mole %	n/m	\bar{a}
0.6	166	333
3.7	26	53
3.8	25	51
4.6	21	43
6.2	15	31
8.2	11	23

Figure Captions

Figure 1. Far infrared spectra of low molecular weight PSMA copolymer and ionomers.

Figure 2. Far infrared spectra of a series of high molecular weight PSMA - Na⁺ ionomers with varying mole % of carboxylic groups.





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